

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 December 2001 (13.12.2001)

PCT

(10) International Publication Number  
**WO 01/94450 A2**

- (51) International Patent Classification: C08J 5/22 (74) Agents: TRECARTIN, Richard, F. et al.; Flehr Hohbach Test Albritton & Harbert LLP, Suite 3400, 4 Embarcadero Center, San Francisco, CA 94111-4187 (US).
- (21) International Application Number: PCT/US01/17675
- (22) International Filing Date: 1 June 2001 (01.06.2001) (81) Designated States (national): AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GR, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/208,746 2 June 2000 (02.06.2000) US (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicants (for all designated States except US): SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025 (US). POLYFUEL, INC. [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): NARANG, Subhash [US/US]; 728 Garland Drive, Palo Alto, CA 94303 (US). VENTURA, Susanne, C. [US/US]; 424 Becker Lane, Los Altos, CA 94022 (US). OLMELJER, David, L. [US/US]; 22 Short Street, San Francisco, CA 94114 (US).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

✱

2c  
1-6, 8, 9

WO 01/94450 A2

(54) Title: POLYMER COMPOSITION

(57) Abstract: The invention includes compositions comprising at least first and second polymers and optionally a third polymer wherein acid subunits, basic subunits and elastomeric subunits are contained in the polymers. In one aspect, the composition comprises a tertiary polymer blend comprising an acidic polymer comprising acidic subunits, a basic polymer comprising basic subunits and an elastomeric polymer comprising elastomeric subunits. In an alternate aspect, the composition comprises a binary polymer blend which comprises acidic or basic subunits in one polymer and a copolymer comprising the other of the acidic or basic subunit and an elastomeric subunit. Such polymer compositions may be formed into a membrane having electrochemical properties which permit the use of such a membrane in an electrochemical device.

## **POLYMER COMPOSITION**

### **TECHNICAL FIELD**

Novel polymer membranes are disclosed which have desirable electrochemical properties rendering them useful in the formation of electrochemical devices such as batteries and fuel cells.

### **BACKGROUND OF THE INVENTION**

Polymer electrolyte membranes are useful in electrochemical devices such as batteries and fuel cells since they function as electrolyte and separator. Such membranes may be readily fabricated as thin flexible films which can be incorporated into cells of variable shape.

Perfluorinated hydrocarbon sulfonate ionomers, such as Nafion® by DuPont or analogous Dow perfluorinated polymers, are presently used as polymer electrolyte membranes for fuel cells. Such prior art membranes, however, have severe limitations when used in hydrogen/air fuel cells and liquid feed direct methanol fuel cells.

Perfluorinated hydrocarbon sulfonate ionomer membranes cannot be operated over a prolonged period of time at temperatures higher than 85°C without showing decomposition and performance degradation. As such, they cannot be used in hydrogen/air fuel cells at 120°C or higher as required to minimize poisoning of the anode catalyst by carbon monoxide which is present when reformat hydrogen gas is used.

Perfluorinated hydrocarbon sulfonate ionomer membranes have also been shown to have high permeability to liquid methanol. Therefore, liquid feed direct methanol polymer electrolyte membrane fuel cells based on Nafion® or similar perfluorinated hydrocarbon sulfonate ionomer membranes have poor efficiency and low power densities.

- 5 Accordingly, it is an object herein to provide polymer membranes which have high proton conductivity, high temperature stability and/or low methanol permeability.

### SUMMARY OF THE INVENTION

The invention includes compositions comprising at least first and second polymers and optionally a third polymer wherein acid subunits, basic subunits and elastomeric subunits  
10 are contained in the polymers.

In one embodiment, the composition comprises a ternary polymer blend comprising an acidic polymer comprising acidic subunits, a basic polymer comprising basic subunits and an elastomeric polymer comprising elastomeric subunits. In some embodiments, one or more of the polymers, preferably the elastomeric polymer, comprises a  
15 semi-interpenetrating network (IPN). In an alternate embodiment, the composition comprises a binary polymer blend which comprises acidic or basic subunits in one polymer and a copolymer comprising the other of the acidic or basic subunit and an elastomeric subunit. Such polymer compositions may be formed into any shape. However, it is preferred that such compositions be formed into a membrane having  
20 electrochemical properties which permit the use of such a membrane in an electrochemical device.

The acidic polymer of the polymer membrane preferably comprises subunits containing sulfonic acid, phosphoric acid or carboxylic acid groups. Sulfonated polyetherether ketone (sPEEK) is the preferred acidic polymer.

25 The basic polymer of the polymer electrolyte membrane preferably comprises subunits containing aromatic amine, aliphatic amine or heterocyclic nitrogen. Polybenzimidazole

(PBI) is an example of a basic polymer. Polyvinylimidazole (PVI) is a preferred basic polymer. The elastomeric polymer is preferably polyacrylonitrile (PAN).

5 In the binary polymer blend, one polymer is an acidic polymer, preferably sPEEK while the second polymer is an elastomeric copolymer, preferably of vinylimidazole and acrylonitrile.

The polymer membrane is preferably permeable to protons but substantially impermeable to organic fuels such as methanol. It also has physical properties which facilitate its use in the fabrication of electrochemical devices and fuel cells.

10 In the case of fuel cells, the polymer membrane can be used in conjunction with other components to form a membrane electrode assembly (MEA). In an MEA, the polymer membrane is combined with a cathode catalyst on one side of the membrane and an anode catalyst on an opposing surface. A cathode electrode and an anode electrode are in electrical contact with the respective catalyst layers. Such an arrangement facilitates catalytic conversion of a fuel such as hydrogen or methanol on the anode side of the MEA to form ionic species such as protons which are transported across the polymer membrane and electrons which are transmitted through the anode electrode to a load and thence to the cathode. On the cathode side of the membrane, the second catalyst facilitates the reduction of an oxidant such as oxygen which forms water by combining with the proton comprising a cationic current across the membrane.

20 The invention further includes electrochemical devices which comprise the polymer membrane of the invention including electrolyzers, batteries, energy storage devices, chemical sensors, electro-chromic devices and fuel cells.

The invention also includes electronic devices which incorporate the fuel cells and the invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically shows a fuel cell incorporating a membrane electrode assembly of the invention. The electrolyte corresponds to a polymer membrane of the invention on which two catalyst layers are formed. The catalyst on the anodic side of the membrane is preferably a platinum ruthenium catalyst while the catalyst on the cathode side is preferably a platinum catalyst. In electrical contact with each of the catalysts are an anode electrode and cathode electrode which act as a means to conduct electrons from the anode to the cathode.

Figure 2 is a cross section of a membrane electrode assembly (without electrodes) which includes the membrane of the invention, the first and second catalyst layers and generally at least one water and gas permeable layer on the cathodic side to provide for the transport of air to and water from the cathode catalyst layer. Generally a carbon paper or carbon cloth is used for such purposes. In addition, a carbon backing is preferably provided on the anode catalyst layer to protect the catalyst layer from damage from the electrodes. Since the backings generally contain conductive material such as carbon, the electrodes can be placed directly on the backing to complete the membrane electrode assembly.

Figure 3 compares the proton conductivity as a function of temperature for the prior art Nafion® membrane as compared to an embodiment of the invention wherein the membrane comprises 81.5% sPEEK, 15.5% PBI and 3% PAN.

Figure 4 shows the thermal stability of a membrane comprising 81.5% sPEEK, 15.5% PBI and 3% PAN. As can be seen, the membrane maintains its mass well above 300°C.

Figure 5 shows the transport of methanol as a function of time across the prior art Nafion® membrane (7 mils thick) as compared to a membrane (5 mils thick) comprising 75% sPEEK, 20% PBI and 5% PAN.

Figure 6 shows the performance of a PEM fuel cell containing the membrane comprising a 75% sPEEK, 20% PBI and 5% PAN. Performance was measured by using hydrogen and air. Anode and cathode catalysts was 1 mg/cm<sup>2</sup> Pt/carbon with Nafion ionomer at 1.5 mg/cm<sup>2</sup> for the anode and 1mg/cm<sup>2</sup> for the cathode. The fuel cell was run at 80°C, 120°C and 140°C. The current density and cell membrane was as follows:

Temperature/°C	current density <u>@0.6V/Acm<sup>-2</sup></u>	Cell resistance <u>@0.6V/ohm</u>
80	0.44	0.036
120	0.65	0.035
140	0.80	0.026

Figure 7 shows the performance of a membrane electrode assembly comprising Pt-Ru catalyst and Pt catalyst layers, fuel cell using 4 molar methanol as organic fuel. (The MEA was prepared with a membrane comprising sPEEK 85.4%, PVI 11.6%, PAN 3%)

#### DETAILED DESCRIPTION OF THE INVENTION

A used herein, the term "acidic polymer" refers to a polymeric backbone which contains one or more acidic subunits. In a preferred embodiment, the backbone contains carbon alone or in combination with oxygen, nitrogen or sulfur. Particularly preferred embodiments include aromatic backbones although aliphatic polymers may also be used. More particularly, an acidic polymer contains acidic subunits which preferably comprise acidic groups including sulphonic acid, phosphoric acid and carboxylic acid groups. Examples of polymers containing sulfonic acid group include perfluorinated sulfonated hydrocarbons, such as Nafion®; sulfonated aromatic polymers such as sulfonated polyetheretherketone (sPEEK), sulfonated polyetherethersulfone (sPEES), sulfonated polybenzobisbenzazoles, sulfonated polybenzothiazoles, sulfonated polybenzimidazoles, sulfonated polyamides, sulfonated polyetherimides, sulfonated polyphenyleneoxide, sulfonated polyphenylenesulfide, and other sulfonated aromatic polymers. The sulfonated aromatic polymers may be partially or fully fluorinated. Other sulfonated polymers include polyvinysulfonic acid, sulfonated polystyrene, copolymers of acrylonitrile and 2-

acrylamido-2-methyl-1 propane sulfonic acid, acrylonitrile and vinylsulfonic acid, acrylonitrile and styrene sulfonic acid, acrylonitrile and methacryloxyethyleneoxypropane sulfonic acid, acrylonitrile and methacryloxyethyleneoxytetrafluoroethylenesulfonic acid, and so on. The polymers may be partially or fully fluorinated. Any class of sulfonated polymer include sulfonated polyphosphazenes, such as poly(sulfophenoxy)phosphazenes or poly(sulfoethoxy)phosphazene. The phosphazene polymers may be partially or fully fluorinated. Sulfonated polyphenylsiloxanes and copolymers, poly(sulfoalkoxy)phosphazenes, poly(sulfotetrafluoroethoxypropoxy) siloxane. In addition, copolymers of any of the polymers can be used. It is preferred that the SPEEK be sulfonated between 60 and 200%, more preferably between 70 to 150% and most preferably between 80 to 120%. In this regard, 100% sulfonated indicates one sulfonic acid group per polymer repeating unit.

Examples of polymers with carboxylic acid groups include polyacrylic acid, polymethacrylic acid, any of their copolymers including copolymers with vinylimidazole or acrylonitrile, and so on. The polymers may be partially or fully fluorinated.

Examples of acidic polymers containing phosphoric acid groups include polyvinylphosphoric acid, polybenzimidazole phosphoric acid and so on. The polymers may be partially or fully fluorinated.

As used herein, a basic polymer refers to a polymeric backbone which contains one or more basic subunits. In a preferred embodiment, the backbone contains carbon alone or in combination with oxygen, nitrogen or sulfur. Particularly preferred backbones include aliphatic backbones although aromatic polymer backbones may also be used. More particularly, a basic polymer contains basic subunits which preferably comprise basic groups such as aromatic amines, aliphatic amines or heterocyclic nitrogen containing groups.

Examples of basic polymers include aromatic polymers such as polybenzimidazole, polyvinylimidazole, N-alkyl or N-aryl polybenzimidazoles, polybenzothiazoles,

- polybenzoxazoles, polyquinolines, and in general polymers containing functional groups with heteroaromatic nitrogens, such as oxazoles, isooxazoles, carbazole, indoles, isoindole, 1,2,3-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,3-triazole, benzotriazole, 1,2,4-triazole, tetrazole, pyrrole, N-alkyl or N-aryl pyrrole, pyrrolidine, N-alkyl and N-arylpyrrolidine, pyridine, pyrazole groups and so on. These polymers may be optionally partially or fully fluorinated.

Examples of aliphatic polyamines include polyethyleneimines, polyvinylpyridine, poly(allylamine), and so on. These basic polymers may be optionally partially or fully fluorinated.

- 10 Polybenzimidazole (PBI) is a preferred basic polymer. Polyvinylimidazole (PVI) is a particularly preferred basic polymer.

- As used herein, an "elastomeric polymer" refers to a polymeric backbone which contains one or more elastomeric subunits. In a preferred embodiment, the backbone contains carbon alone or in combination with oxygen, nitrogen, fluorine or sulfur. Particularly preferred embodiments include aliphatic backbones although aromatic polymer backbones may also be used. More particularly, an elastomeric polymer comprises elastomeric subunits which preferably contain elastomeric groups such as nitrile, vinylidene fluoride, siloxane and phosphazene groups. Examples of elastomeric polymers include polyacrylonitrile, acrylonitrile copolymers, polyvinylidene fluoride, vinylidene fluoride copolymers, polysiloxanes, siloxane copolymers and polyphosphazenes, such as poly(trifluoromethylethoxy)phosphazene.

The elastomeric polymer may be added to the polymer membrane in the form of polymerizable monomer to fabricate semi-interpenetrating networks. The monomers may be polymerized photochemically or by thermal treatment for the semi-IPN.

- 25 As used herein, an elastomeric copolymer refers to an elastomeric polymer which contains elastomeric subunits and one or more acidic subunits or basic subunits

depending upon which embodiment of the invention is being practiced. For example, if an acidic polymer such as sPEEK is used, an elastomeric copolymer comprising elastomeric subunits and basic subunits may be used in a binary composition.

- 5 Alternatively, should a basic polymer be used, the elastomeric copolymer will comprise elastomeric subunits and acid subunits. Such binary mixtures may be used in conjunction with other polymers and copolymers to form additional compositions within the scope of the invention.

- 10 The acid equivalent weight of the polymer containing the acid group (sulfonic acid, carboxylic acid and/or phosphoric acid) is selected within a suitable range to provide high proton conductivity. When used in a ternary blend, *i.e.*, a mixture of an acidic polymer, a basic polymer and an elastomeric polymer. The acid polymer will be used in the composition in a concentration varying from 10% to 99% by weight, more preferably 30 to 95% by weight and most preferably between about 50 and 90% by weight.

- 15 The function of the polymer containing the basic functional group is to form pseudo crosslinking with the polymer containing the acid group via acid-base interaction. Pseudo crosslinking is needed to prepare films that are mechanically stable at high humidities and in boiling water. When used in a ternary blend, the basic polymer will be used in the composition in a concentration varying from 0.5% to 50% by weight, more preferably between 2.5 to 40 % by weight, still more preferably between about 5 and 25% by weight.

- 20 The function of the elastomeric polymer is to allow the fabrication of polymer membranes with superior mechanical properties as well as membranes having low methanol permeability. The elastomeric polymer will be used in concentration varying from 0.5% to 50% by weight, more preferably between 2.5 to 40% by weight and most preferably between about 5 and 25% by weight.

- 25 In a particularly preferred embodiment, the ternary blend membrane contains sulfonated polyetheretherketone (sPEEK) as acidic polymer, polyvinylimidazole (PVI) as a basic polymer and polyacrylonitrile (PAN) as elastomeric polymer. In the best mode of

practicing the invention, this composition contains 85.4% sPEEK by weight, 11.6% PVI by weight and 3% PAN by weight.

In those embodiments, when the composition comprises two polymers, i.e., in a binary blend, the acid polymer can constitute any one of the aforementioned acidic polymers. It is preferred that when an acidic polymer is chosen, that the polymer be sPEEK. In such circumstances, the second polymer comprises an elastomeric copolymer containing elastomeric subunits and basic subunits. In this embodiment, the basic subunit is preferably vinylimidazole and the elastomeric subunit is acrylonitrile. While good membranes can be obtained with such a binary system, a basic polymer may optionally be added. When so used, it is preferred that polyvinylimidazole be used although polybenzimidazole may also be used.

In the composition comprising a binary polymer blend, wherein an acidic polymer is used, it is preferred that the acidic polymer comprise sPEEK. It is also preferred that the acidic polymer have a concentration of between about 10 to 99%, more preferably between 30 to 95% and most preferably between 50 to 90%. In addition, it is preferred that the elastomeric copolymer containing a basic subunit be present at a concentration of between 1 to 90%, more preferably between 5 to 70% and most preferably between 10 to 50%. The foregoing concentrations of the elastomeric copolymer are for situations wherein the elastomeric copolymer comprises about 50% elastomeric subunits. However, the amount of elastomeric copolymer will vary depending upon the base content of the elastomer copolymer. In general, the lower the base content of the elastomeric copolymer, the higher the amount of copolymer which can be used. Similarly, a reduction in the amount of basic subunit results in a higher level of copolymer which can be used. Preferred ranges for basic/elastomer subunits in the copolymer are from 99:1 to 1:99.

When a basic polymer is used in the binary polymer blend, it is preferred that the basic polymer be polybenzimidazole and most preferably polyvinylimidazole. Generally the basic polymer will be present at a concentration of about between 1 to 90 weight percent,